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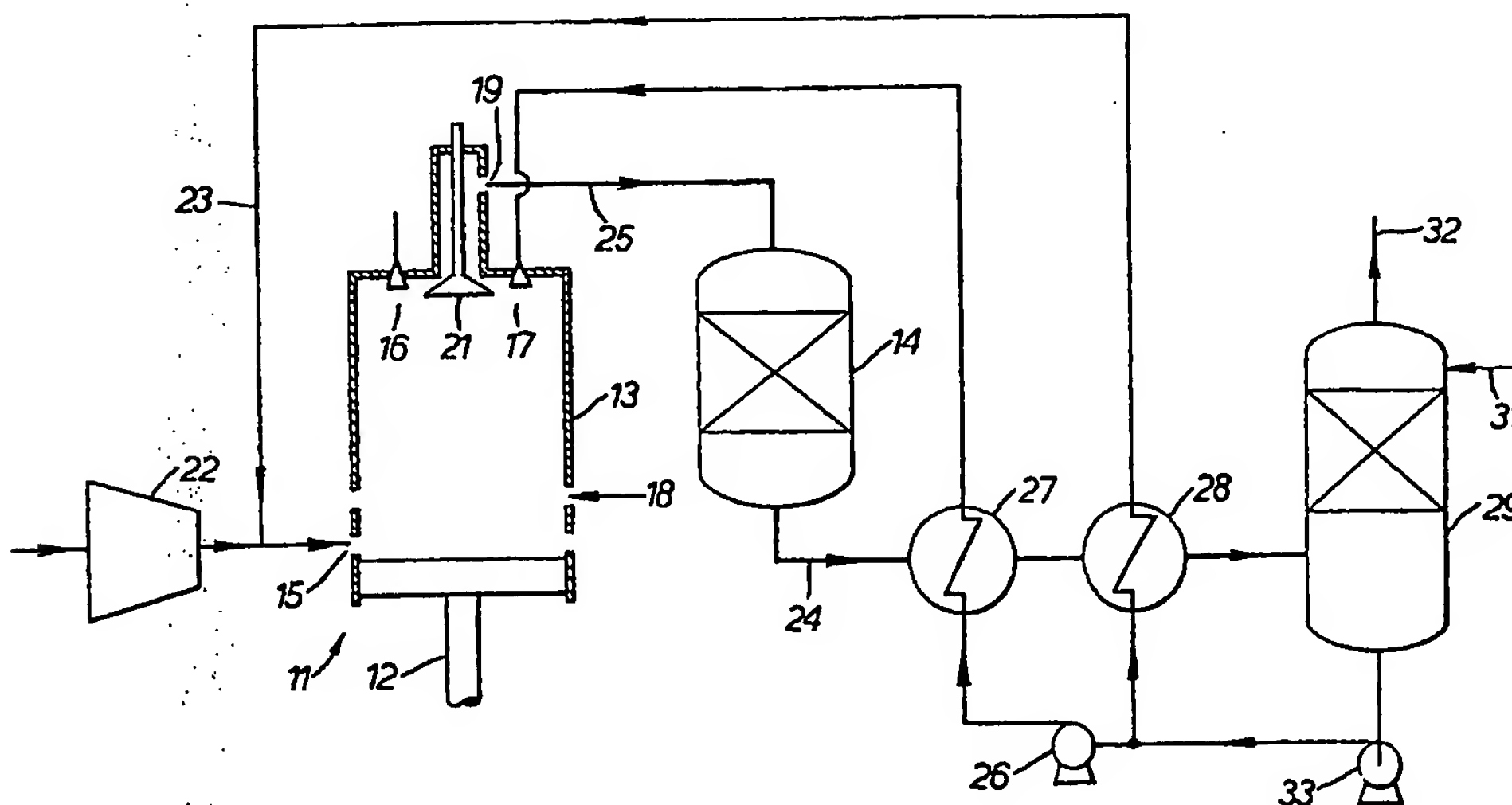F02B 47/02 F02B 47/06 // 45/02

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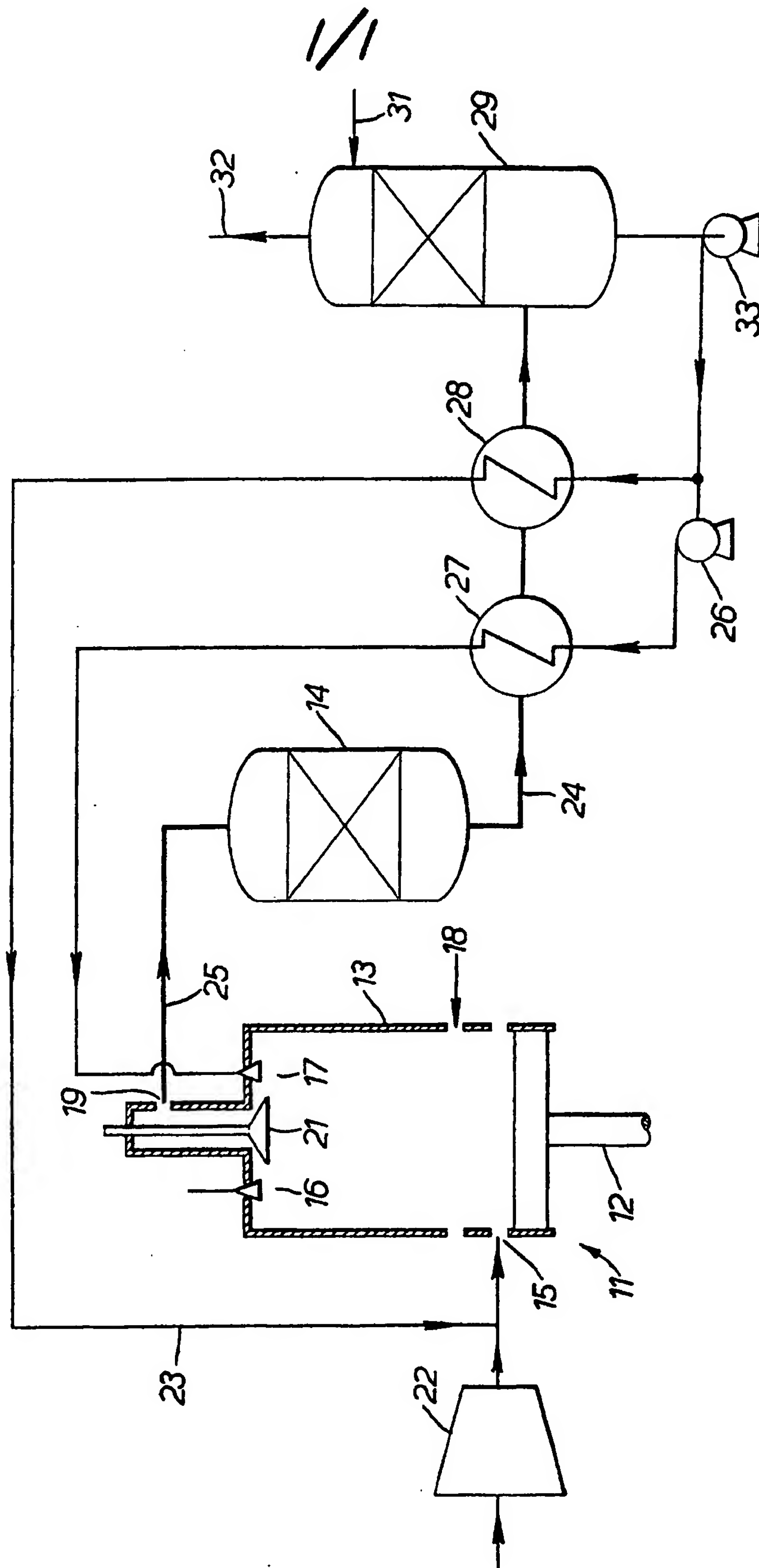GB 0807051   GB 0705514

(58) Field of search
F1B

(54) Production of synthesis gas using an I.C. engine

(57) Synthesis gas comprising essentially carbon monoxide and hydrogen is produced by introducing hydrocarbon fuel 16, oxygen/steam 15 and optionally hot water 17 to an internal combustion engine 11. The amounts of steam, oxygen and water are arranged so that partial oxidation of the fuel takes place. The engine simultaneously produces useful work that may be used to generate electric power and synthesis gas with a minimum of low grade heat being produced. A portion of the carbon monoxide produced is reacted with steam in a shift reactor 14 to produce CO_2 and hydrogen.

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The drawing(s) originally filed was (were) informal and the print here reproduced is taken from a later filed formal copy.

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SPECIFICATION

Process for the production of synthesis gas

5 The present invention relates to a process for producing a mixture of hydrogen and carbon monoxide, commonly referred to as synthesis gas from a hydrocarbon fuel. The term hydrocarbon fuel as used herein is intended to include combustible
10 fuels composed of and including hydrocarbons and also slurries of coal, coke etc. in water and also gaseous hydrocarbons.

It is known that to break the bond holding a hydrogen atom in a molecule either by electrolytic
15 means in the case of water or by thermal means in the case of a hydrocarbon, requires a strong force. In the case of thermal treatment as applied to hydrocarbons, the bond is commonly broken by means of high temperatures in conjunction with a
20 catalyst and steam, a process commonly known as steam reforming, or by means of high temperatures in conjunction with oxygen, commonly referred to as partial oxidation. Partial oxidation is essentially effected by providing fuel in excess of
25 the stoiciometric quantity required for complete combustion with the result that carbon monoxide is primarily formed as opposed to carbon dioxide.

By either route, a mixture of hydrogen and carbon monoxide is produced. With the aid of steam
30 and a second catalyst, the carbon monoxide can be oxidised further with the oxygen component of steam to produce hydrogen and carbon dioxide, a process commonly called shift conversion.

In both of the above routes for making synthesis
35 gas from a hydrocarbon feedstock, the chemical reaction is rapid once the necessary high temperature is attained. It is important that once the reaction has occurred, the products are rapidly cooled from temperatures which may be as high as
40 1400°C down to 350°C. This is achieved either by direct or indirect quench means or a combination of both, depending upon the particular process route chosen.

Due to the high temperatures required to break
45 the hydrogen atomic bond and the need subsequently to cool the reacted products quickly, both described commonly used process routes require a large heat energy input of which a large proportion can only be recovered in the form of low grade
50 heat or as steam. Thus, inherently, both these process routes may be described in thermodynamic terms as being relatively inefficient.

It is an object of the present invention to provide a process for the manufacture of synthesis gas
55 having an improved thermodynamic efficiency.

According to the invention there is provided a process for the production of synthesis gas from a hydrocarbon fuel which comprises introducing oxygen and steam to an internal combustion engine;
60 compressing the oxygen and steam in a compression stage thereby raising the temperature to a level at which ignition of the hydrocarbon fuel can occur; introducing the hydrocarbon fuel to the engine; allowing ignition of the hydrocarbon fuel to
65 take place in an ignition stage, and allowing com-

bustion and expansion of the gases to take place in a combustion/expansion stage, the amount of oxygen introduced being such as to cause only partial oxidation of the fuel on combustion whereby the
70 exhaust gases from the engine comprise essentially carbon monoxide, hydrogen and steam with relatively small amounts of oxygen and carbon dioxide.

The compression ratio of the steam/oxygen mix-
75 ture may be between 12:1 and 18:1, and preferably, the temperature, after ignition, also enables a portion of the fuel to react with the steam to produce carbon monoxide and hydrogen.

Preferably, the exhaust gases from the engine
80 are introduced to a shift reactor in which a portion of the carbon monoxide and steam react over a catalyst to form carbon dioxide and hydrogen. Preferably, useful work is done by the engine during the combustion/expansion stage as a result of the
85 rapid rise in pressure whilst simultaneously reducing the temperature of the reacted gases towards a temperature which is suitable for a subsequent shift conversion. The maximum pressure may be between 90 and 150 bars.
90 Preferably, the amount of steam mixed with the oxygen prior to their being introduced into the engine is such that the proportions are suitable for a subsequent shift conversion. Alternatively, water may be injected directly into the engine and the
95 proportion of steam is suitably reduced such that the mixture leaving the engine is at a temperature and in suitable proportions for a subsequent shift conversion. In the latter case, the injection water is preferably preheated to between 200 and 300°C by
100 heat exchange against either the engine discharge or a shift reactor discharge.

The steam required may be raised in a steam generator by indirect heat exchange of the process water with the shift reactor discharge. Preferably,
105 the process water is first directly heat exchanged against the reacted gases in a direct contact tower, after the gases have left the steam generator thereby simultaneously preheating the process water and condensing out a substantial proportion
110 of any unreacted steam in the reacted gas stream.

In a preferred embodiment, a first portion of the heated process water from the direct contact tower is pumped to the steam generator to raise steam for the process and a second portion is heat ex-
115 changed either against the engine or shift reactor discharge prior to its being directly injected into the engine. Optionally, a small amount of steam or carbon dioxide is separately introduced into the engine at the beginning of the compression stroke
120 to act as a buffer between the partially oxidised reactants discharging from the cylinder and the fresh steam-oxygen mixture entering the cylinder.

The steam/oxygen mixture may be introduced into the engine at ambient pressure or at a pres-
125 sure above ambient.

The fuel may be hot liquid bitumen, or a slurry of petroleum coke or coal in hot liquid bitumen, or a reduced crude oil, heavy fuel oil or gas oil, or a slurry of petroleum coke or coal in water.
130 Thus, it has been found that by mixing oxygen

and steam at essentially atmospheric pressure in approximately 5. stoiciometric proportions for a subsequent shift conversion and compressing these in an internal combustion engine capable of
5 accommodating high combustion pressures, temperatures necessary to initiate the partial oxidation reaction can be achieved, i.e. around 400°C.

It has also been found that when a hydrocarbon fuel is injected into such an engine containing such
10 an oxygen-steam mixture, after the initiation of partial oxidation producing a mixture essentially comprising hydrogen, carbon monoxide, steam and some carbon dioxide, due to the resultant high temperature of around 1400°C, and the formation
15 or presence of some particulate carbon from the hydrocarbon fuel, the well known water gas reaction, producing carbon monoxide and hydrogen, also occurs. This reaction is known to be endothermic and has the effect of reducing the maximum
20 temperature in the engine, which is beneficial.

During the expansion stroke of the engine, work is done in excess of that required for compression and after the near total consumption of the oxygen, the temperature of the reacted gases de-
25 creases as work is performed by the engine. A nett amount of useful work may thus be recovered from the engine while at the same time producing a synthesis gas mixture and cooling the reacted constituents towards a temperature which is suita-
30 ble for a subsequent shift conversion. The useful work may be used to drive an electric generator.

This may represent a substantial thermodynamic improvement in the production of synthesis gas as opposed to simply quenching the reaction prod-
35 ucts and removing excess heat in the form of low grade heat or indirectly raising steam.

The resultant temperature of the partial oxidation reaction, if effected at essentially constant pressure, may be about 1400°C, when the feedstock
40 constituents have been pre-heated to between 400 and 600°C and up to 5% of the supply oxygen over-burns to produce carbon dioxide. The oxidation of carbon to carbon dioxide releases considerably more heat than the oxidation of carbon to
45 carbon monoxide but is generally not desired where the objective is to make synthesis gas or to maximise subsequent hydrogen production.

Thus, when the reactions in accordance with the invention occur in an internal combustion engine
50 under controlled conditions and the work done by such an engine is equivalent to around 40% of the energy released by the fuel due to the partial oxidation reaction, the final discharge temperature of the mixture from the engine may be about around
55 400°C, after allowing for the cooling applied to the engine components and the heat consumed in the endothermic water gas reaction. However, if a small portion of the fuel is oxidised directly to produce carbon dioxide, which releases considerably
60 more heat, the final discharge temperature can be higher, e.g. around 600°C.

It is preferable when effecting the shift reaction (which is commonly effected in two stages since it is 7. slightly exothermic) that the inlet temperature
65 to the shift reactor should be around 375°C or less

with more reactive catalyst.

It has been found that, by injecting clean water directly into such an internal combustion engine, the discharge temperature can be conveniently
70 controlled within the temperature range of 300 to 400°C, which is suitable for a subsequent shift conversion reaction without further cooling. It has also been found that by injecting clean water directly into such an engine, the cooling effect can be used
75 to influence the various above-described oxidation reactions which occur as well as to limit the maximum temperature. It has further been found that, by reducing the quantity of steam in the initial oxygen-steam mixture in proportion to the amount of
80 water injected directly into the machine, the nett work done by the engine can be increased primarily due to the reduction of irreversible energy losses attributable to the compression stroke.

Shift conversion tends to be only slightly exoth-
85 ermic with the result that the temperature change across a shift reactor is small, and so the resultant discharge temperature is generally in the same range as the inlet gas temperature. It has been found that the remaining heat in the gases leaving
90 the shift reactor may be adequate to raise a substantial amount of steam at around 2.0 bar by indirect heat exchange means and, in some cases may be sufficient to raise the amount required to satisfy the shift reaction requirement over a wide range of
95 hydrocarbon fuels.

The process may in fact be balanced so that by varying the relative quantity of fuel injected into the engine in proportion to the oxygen-steam supply necessary to favour the preferred oxidation re-
100 actions described above, and by varying the amount of water directly injected into the engine in relation that required to control the engine outlet temperature, variable amounts of steam can be raised to accommodate variable degrees of shift
105 conversion as may be required for any subsequent process objectives, and the amount of heat energy consumed within the process as a whole can be minimised. Such subsequent process objectives may be to make methanol, synthetic gasoline or to
110 maximise production of hydrogen. In each case, the required proportion of carbon monoxide to hydrogen is different.

It has also been found that the process may, in fact accommodate a wide range of fluid hydrocar-
115 bon fuels. Some may be as heavy as hot liquid bitumen containing only 8 or 10% by weight of hydrogen and in some cases that the amount of low grade heat removed from the process may be reduced towards zero.
120 In some cases, the process can accommodate hydrocarbon fuels comprising a slurry of liquid and solids, such as slurry of petroleum coke or coal in hot liquid bitumen subject to the fuel injection means into the internal combustion engine and
125 other mechanical features of a particular engine being able to accommodate such fuels. It has also been found that a solid fuel such as petroleum coke or coal in a slurry of water may be injected into the engine and partially oxidised subject to a
130 particular engine being able to accommodate such

a fuel. In such a case, the water directly injected into the engine would be proportionately reduced to balance the amount mixed with the fuel.

5 When fuel containing sulphur is injected into the engine, a proportion converts to hydrogen sulphide as a side reaction. This may be subsequently removed by one of a number of well established methods.

10 With the established partial oxidation processes even with considerable feedstock pre-heat, it is common practice to over-burn a small portion of the fuel to carbon dioxide, e.g. around 5%, to achieve the temperatures necessary to make the partial oxidation reactions take place, also that

15 some fuel passes out of the reaction chamber in the form of particulate carbon. A secondary benefit of the present invention is that over-burn can be minimised and, in some cases, avoided altogether. Also, due to the high temperatures that may be at-

20 tained in high combustion pressure tolerant internal combustion engines, the amount of particulate carbon leaving in the discharge gas may be reduced. However, in certain circumstances, a small amount of over-burn may be desirable, for exam-

25 ple, where it is required to produce more power or to minimise the amount of fuel which leaves the engine in the form of particulate carbon, especially with the heaviest fuels.

It has been found that, whereas the quantity of

30 hydrogen produced is reduced with fuel over-burn, the useful work done by the same engine may be increased. For example, when using a heavy fuel at 5% over-burn, the hydrogen production is reduced by 4% but the useful work done by the same en-

35 gine can increase by 6% when water is directly injected into the engine and the steam content of the supply oxygen-steam mixture is proportionally reduced.

The timing and period of exhaust valve opening

40 should be adjusted to release the maximum quantity of reacted products from the engine but to minimise the quantity of by-pass oxygen-steam mixture passing through the engine without being subjected to partial oxidation. Care has to be taken

45 to minimise the amount of oxygen thus passing out of the engine. This can be minimised when only steam is initially allowed to enter the engine cylinder during the scavenging phase, in effect, to act as a buffer between the inlet oxygen-steam

50 mixture and discharging partially combusted products. Alternatively, a portion of carbon dioxide may be substituted for the steam.

The invention may be carried into practice in various ways and one embodiment will now be de-

55 scribed, by way of example with reference to the accompanying drawings in which the single figure is a schematic process diagram based on a uniflow, scavenged two-stroke slow speed diesel engine, although other types of internal combustion

60 engine may be suitable.

The apparatus for carrying out the process includes an engine 11 having a piston 12 in a cylinder 13, and a shift reactor 14. The cylinder 13 includes an oxygen/steam inlet 15 near the bottom,

65 a fuel inlet 16, a hot water inlet 17, an optional CO_2

steam inlet 18 and an exhaust port 19 controlled by an exhaust valve 21.

The oxygen is supplied to the cylinder 13 by means of a turbo-blower 22 and is mixed with a

70 supply of low pressure steam, from line 23, raised by means of heat exchange against the discharge 24 from the shift reactor 14 and enters via the inlet 15. The oxygen steam mixture temperature should be above the water dew point, preferably around

75 100°C at 1.5 bars pressure. A small amount of secondary steam or carbon dioxide enters the cylinder 13 either by the same inlet 15, or via the optional inlet 18, to act as a buffer between the supply oxygen-steam mixture and the discharging partially

80 oxidised fuel.

When the piston 12 has reached top dead centre, fuel injection via the fuel nozzle 16 is initiated. Fuel injection should be preferably rapid and well dispersed to favour the partial oxidation reactions.

85 Clean hot water may be injected through the water inlet 17 at a rate which may be varied, depending on the engine design, to favour the partial oxidation reaction that occurs at a temperature around 1400°C. This will cause the discharge tem-

90 perature at the completion of the expansion stroke to be around 400°C.

Because there is a considerable increase in the molal ratio of the reacted products to the supply oxygen steam mixture and volume expansion, due

95 to the heat of reaction, the supply mixture compression ratio in the engine would normally be between 12 and 16, to result in a maximum combustion-pressure of around 120 bars. Towards completion of the partial oxidation reactions, the

100 resultant temperature will be between 12. 1200 and 1700°C, subject to only a minimum of useful work being done by the engine. These high temperatures only exist for a brief period of perhaps less than one second and rapidly decrease to between

105 300 and 600°C as the engine piston 12 travels through its expansion stroke, doing useful work.

The final discharge temperature will be dependent on a number of factors, including, but not limited to, the thermal efficiency of a particular

110 engine, type of fuel, over-burn, inlet oxygen-steam mixture temperature and amount of directly injected clean water.

The exhaust valve 21 opens towards the completion of the combustion/expansion stroke and the

115 reacted gases are discharged via a conduit 25 and passed to the shift reactor 14 where the carbon monoxide may be reacted with steam to produce more hydrogen and carbon dioxide.

Clean water is injected into the engine by means

120 of a high pressure water injection pump 26 via the water inlet spray nozzle 17 after being heated by heat exchange against the shift reactor discharge stream 24 in a heat exchanger 27. After the heat exchanger 27, the gases in the discharge stream 24

125 are heat exchanged with a portion of the process water in a steam generator 28. The steam raised in the steam generator 28 is mixed with the oxygen via the steam line 23.

Upon leaving the steam generator 28, at around

130 130°C the gases are passed to a quench tower 29

to cool the gases further and to condense out as much remaining water vapour as possible against a clean water inlet 13. stream 31, before being passed to further processing through conduit 32.

5 Hot water from the quench tower 29, together with clean water used as coolant within the engine itself and any make-up, is passed to the steam generator 28 via a pump 33. The clean injection water may be pre-heated to around 250°C against the engine

10 discharge stream 25 as a means of further control over the shift reactor inlet temperature or against the shift reactor discharge 24 as shown in Figure 1 in the heat exchanger 27, thus further improving the thermal efficiency of the process.

15
CLAIMS

1. A process for the production of synthesis gas from a hydrocarbon fuel which comprises intro-

20 ducing oxygen and steam to an internal combustion engine; compressing the oxygen and steam in a compression stage thereby raising the temperature to a level at which ignition of the hydrocarbon fuel can occur; introducing the hydrocarbon fuel to

25 the engine; allowing ignition of the hydrocarbon fuel to take place in an ignition stage, and allowing combustion and expansion of the gases to take place in a combustion/expansion stage, the amount of oxygen introduced being such as to

30 cause only partial oxidation of the fuel on combustion whereby the exhaust gases from the engine comprise essentially carbon monoxide, hydrogen and steam with relatively small amounts of oxygen and carbon dioxide.

35 2. A process as claimed in Claim 1 in which the compression ratio of the steam-oxygen mixture is between 12:1 and 18:1.

3. A process as claimed in Claim 1 or Claim 2 in which the temperature, after ignition, also enables

40 a portion of the fuel to react with the steam to produce carbon monoxide and hydrogen.

4. A process as claimed in any preceding Claim in which the exhaust gases from the engine are introduced to a shift reactor in which a portion of the

45 carbon monoxide and steam react over a catalyst to form carbon dioxide and hydrogen.

5. A process as claimed in any preceding claim in which useful work is done by the engine during the combustion/expansion stage as a result of the

50 rapid rise in pressure, whilst simultaneously reducing the temperature of the reacted gases towards a temperature which is suitable for a subsequent shift conversion.

6. A process as claimed in any preceding Claim

55 in which maximum pressure is between 90 and 150 bars.

7. A process as claimed in any preceding claim in which the amount of steam mixed with the oxygen prior to their being introduced into the engine

60 is such that the proportions are suitable for a subsequent shift conversion.

8. A process as claimed in any of Claims 1 to 6 in which water is injected directly into the engine and the proportion of steam is suitably reduced

65 such that the mixture leaving the engine is at a

temperature and in suitable proportions for a subsequent shift conversion.

9. A process as claimed in Claim 8 in which the injection water is preheated to between 200 and

70 300°C by heat exchange against either the engine discharge or a shift reactor discharge.

10. A process as claimed in any of Claims 4 to 8 in which the steam required by the process is raised in 16 a steam generator by indirect heat ex-

75 change of the process water with the shift reactor discharge.

11. A process as claimed in Claim 10 in which the process water is first directly heat exchanged against the reacted gases, in a direct contact tower,

80 after the gases have left the steam generator thereby simultaneously preheating the process water and condensing out a substantial proportion of any unreacted steam in the reacted gas stream.

12. A process as claimed in Claim 11 in which a

85 first portion of the heated process water from the direct contact tower is pumped to the steam generator to raise steam for the process and a second portion is heat exchanged either against the engine or shift reactor discharge prior to its being directly

90 injected into the engine.

13. A process as claimed in any preceding Claim in which a small amount of steam or carbon dioxide is separately introduced into the engine at the beginning of the compression stroke to act as a

95 buffer between the partially oxidised reactants discharging from the cylinder and the fresh steam-oxygen mixture entering the cylinder.

14. A process as claimed in any preceding Claim in which the steam-oxygen mixture is intro-

100 duced into the engine substantially at ambient pressure.

15. A process as claimed in any of Claims 1 to 13 in which the steam-oxygen mixture is introduced into the engine at a pressure higher than

105 ambient but less than 5 bars.

16. A process as claimed in any preceding Claim in which the fuel is hot liquid bitumen, or a slurry of petroleum coke or coal in hot liquid bitumen.

110 17. A process as claimed in any of Claims 1 to 15 in which the fuel is a reduced crude oil, heavy fuel oil or gas oil.

18. A process as claimed in any of Claims 1 to 15 in which the fuel is a slurry of petroleum coke

115 or coal in water.

19. A process as claimed in any of Claims 1 to 15 in which the fuel is a gaseous hydrocarbon.

20. A process for the production of synthesis gas from a hydrocarbon fuel substantially as

120 herein specifically described with reference to and as shown in the accompanying drawing.